#### (19) World Intellectual Property Organization International Bureau



# 

#### (43) International Publication Date 11 July 2002 (11.07.2002)

#### **PCT**

### (10) International Publication Number WO 02/053359 A1

(51) International Patent Classification7: B29C 65/04, A61L 29/12, C08L 23/10 B32B 1/08,

TERNATIONAL INC., One Baxter Parkway, Deerfield, IL

- (21) International Application Number: PCT/US02/00299
- (22) International Filing Date: 4 January 2002 (04.01.2002)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 09/756,490

8 January 2001 (08.01.2001)

- BAXTER INTERNATIONAL INC. [US/US]; One Baxter Parkway, 2-2E, Deerfield, IL 60015
- (72) Inventors: LING, Michael T., K.; 1672 Cypress Pointe Drive, Vernon Hills, IL 60061 (US). HURST, William, S.; W650 Spring Prairie Rd., Burlington, WI 53105 (US). WOO, Lecon; 1013 Shari Lane, Libertyville, IL 60048 (US). BINDOKAS, Algirdas; 67 Waverly Avenue, Clarendon Hills, IL 60514 (US). RYAN, Patrick, T.; 968 Boxwood Drive, Crystal Lake, IL 60014 (US). EDWARDS,

Scott, D.; 1124 Jaimee Lane, Libertyville, IL 60048 (US). BLOM, Henk, P.; 430 W. Northshore Drive, Mundelein, IL 60060 (US). KHARE, Atul, R.; 1529 Magnolia Drive, Crystal Lake, IL 60014-1983 (US).

(74) Agents: BUONAIUTO, Mark, J. et al.; BAXTER IN-

- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

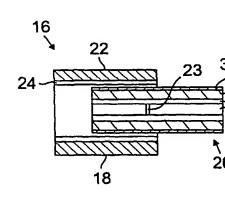
#### Published:

60015 (US).

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PORT TUBE AND CLOSURE COMPOSITION, STRUCTURE AND ASSEMBLY FOR A FLOWABLE MATERIAL CONTAINER



(57) Abstract: The present invention provides a flowable material container closure assembly having a port tube and a membrane tube. The port tube has a first layer and a second layer, the first layer is a polymer blend and the second layer is disposed coaxially within the first layer; and the membrane tube is disposed coaxially within the port tube, the membrane tube has an outer layer, a core layer and an inner

Ġ,

WO 02/053359

-1-

# PORT TUBE AND CLOSURE COMPOSITION, STRUCTURE AND ASSEMBLY FOR A FLOWABLE MATERIAL CONTAINER

#### **DESCRIPTION**

#### TECHNICAL FIELD:

5

10

15

20

25

The present invention relates generally to closures for flowable material containers and more particularly port tube assemblies for medical fluid containers.

#### BACKGROUND OF THE INVENTION:

It is common medical practice to provide fluids to a patient either intravenously or enterally as a method of treating a patient for various medical conditions. Frequently, the fluids to be administered to a patient are contained in a flexible container. One method of forming a flexible container is to seal two sheets of flexible material about the periphery of the sheets to create a fluid tight chamber. A port tube assembly is frequently placed between the sheets during the sealing process to create a communication between the fluid chamber and the exterior of the container to provide a means of introducing fluid into or dispensing fluid from the container. The port tube assembly typically includes an outer port tube that attaches to the sidewalls of the container and a second tube called a membrane tube is disposed coaxially within the port tube. The membrane tube has a membrane or diaphragm that seals the port tube assembly. The membrane is typically punctured by a spike of a fluid administration set to place the contents of the container in fluid communication with a patient.

Port tubes and membrane tubes are fabricated from monolayer or multiple layered materials. The port tube typically has an inner layer of polyvinyl chloride and the membrane tube has an outer layer of PVC. To assemble the port tube assembly, the membrane tube is dipped in cyclohexanone or other suitable solvent and is inserted in a telescoping fashion into the port tube. The solvent melts the PVC of both the port tube and the membrane tube thereby hermetically sealing the membrane tube to the port tube.

There has been a great effort by many manufacturers of medical articles to replace PVG materials with non-PVC containing materials. Flexible PVC containers include low molecular weight additives know as plasticizers which may exude into the solutions contained in the container. United States Patent Nos. 5,998,019 and 5,849,843, which are incorporated herein by reference and made a part hereof, disclose replacing PVC materials in medical fluid containers with

٠.,٠

- 2 -

.

學生學

non-PVC containing materials.

5

10

15

20

25

30

United States Patent No. 5,356,709, assigned to the same assignee of the present invention, discloses a non-PVC coextruded medical grade port tubing. The tubing has an outer layer of a blend of polypropylene and SEBS a tie layer and a core layer of a blend of polyamide and EVÄY.

United States Patent No. 5,533,992, assigned to the same assignee of the present invention; discloses a non-PVC material for fabricating medical tubings and medical containers. Polymer blends for fabricating medical tubing disclosed in the '992 Patent include polyurethane blended with one or more of the following: EVA, SEBS, PCCE, thermoplastic copolyester elastomers.

#### SUMMARY OF THE INVENTION:

The present invention provides a non-PVC port tube, a non-PVC membrane tube and a non-PVC port tube assembly for use in flowable material containers such as medical and food containers.

The closure assembly includes a port tube and a membrane tube coaxially mounted therein The port tube has a first layer and a second layer. The first layer is a multiple component polymer blend having a first component in an amount by weight of from about 25% to about 50% by weight of the first layer. The first component is a first polyolefin selected from the group consisting of polypropylene and polypropylene copolymers. The second component is present in an amount by weight of from about 0% to about 50% by weight of the first layer and is a second polyolefin. The second polyolefin is selected from the group consisting of ethylene copolymers, ultra-low density polyethylene, polybutene, polybutadiene and butene ethylene copolymers. The third component is present in an amount by weight of from about 0% to about 40% by weight of the first layer and is a radio frequency ("RF") susceptible polymer. The RF polymer is selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers; polyimides, polyurethanes, polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene methyl acrylate copolymers with methyl acrylate comonomer content from 12%-40% by weight of the copolymers ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer. The fourth component is present in an amount from about 0% to about 40% and is a first thermoplastic elastomer.

The second layer of the port tube is disposed coaxially within the first layer and in a preferred form of the invention is a polymeric material that is susceptible of solvent bonding and

5

10

15

20

25

30

1. .

· ; já

more preferably includes a second thermoplastic elastomer. Optionally, the second layer can include an additive from about 0% to about 20% by weight of a polypropylene, high density polyethylene, silica, slip agents, fatty amides, acrawax and the like.

The membrane tube has an outer layer, a core layer and an inner layer. The outer layer of the membrane tube is capable of being solvent bonded to the second layer of the port tube. In a preferred form of the invention, the outer layer of the membrane tube (A) is a polymer blend of:

(1) from about 0% to about 60% by weight of the outer layer of a third polyolefin and (2) from about 40% to about 100% by weight of the outer layer of a second component of a third thermoplastic elastomer. The core layer (B) is attached to the outer layer. In a preferred form of the invention, the core layer is a polymer blend of: (1) from about 35% to about 100% by weight of the core layer of a fourth thermoplastic elastomer and (2) from about 0% to about 65% by weight of the core layer of a fourth polyolefin.

The inner layer of the membrane tube is attached to the core layer on a side opposite of the outer layer. The inner layer is a multiple component polymer blend of and in a preferred form has: (1) from about 25% to about 55% by weight of the inner layer a fifth polyolefin, (2) from about 0% to about 50% by weight of the inner layer a sixth polyolefin selected from the group consisting of ethylene copolymers, ultra-low density polyethylene, polybutene, and butene ethylene copolymers; (3) from about 0% to about 40% by weight of the inner layer of a radio frequency susceptible polymer selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, polyimides, polyurethanes, polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene with methyl acrylate comonomer content from 12%-40% by weight of the copolymer, ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer; and (4) from about 0% to about 40% by weight of the inner layer of a fifth thermoplastic elastomer.

These and other aspects and attributes of the present invention will be discussed with reference to the following drawings and accompanying specification.

## BRIEF DESCRIPTION OF THE DRAWINGS:

FIG. 1 is a plan view of a flowable material container with port closure assembly; and FIG. 2 is a cross-sectional view of a port tube of the present invention.

- 4 -

#### DETAILED DESCRIPTION OF THE INVENTION

5

10

15

20

25

30

The present invention is susceptible of embodiments in many different forms. Preferred embodiments of the invention are disclosed with the understanding that the present disclosure is to be considered as exemplifications of the principles of the invention and are not intended to limit the broad aspects of the invention to the embodiments illustrated.

FIG. 1 shows a flowable material container 10 having sidewalls 12 sealed along peripheral edges to define a chamber 14 therebetween. A port tube closure assembly 16 provides access to the contents of the container. The container 10 is preferably fabricated from a non-PVC containing material. In a preferred form of the invention, the sidewalls 12 are fabricated from a multiple component polymer alloy such as those disclosed in detail in U.S. Patent No. 5,686,527 which is incorporated herein by reference and made a part hereof. One particularly suitable polymer alloy is a blend of polypropylene, ultra-low density polyethylene, a polyamide and a styrene and hydrocarbon block copolymer. The container 10 shown in FIG. 1 is particularly suitable for medical applications such as storage and delivery of I.V. solutions, peritoneal dialysis solutions, pharmaceutical drugs and blood and blood components to name a few. It is contemplated that such a container can also be used to store food products, serve as a drain bag for peritoneal dialysis or store other consumable products.

What is meant by "flowable material" is a material that will flow by the force of gravity: Flowable materials therefore include both liquid items and powdered or granular items and the like:

FIG. 2 shows the port tube assembly 16. The port tube assembly 16 has a port tube 18 and a membrane tube 20 coaxially mounted therein. A fluid passageway 22 of the membrane tube 20 is sealed by a membrane 23 positioned at an intermediate portion of the membrane tube 20. For medical applications, the membrane 23 can be punctured by a spike of an infusion set to place the contents of the container into fluid communication with, for example, the vascular system of a patient being treated.

In a preferred form of the invention, the port tube 18 is a multilayered structure and more preferably has a first layer 22 and a second layer 24. The first layer 22 should be of a non-PVC containing material that is capable of being sealed to the sidewalls 12 of the container 10, and preferably sealed using radio frequency sealing techniques. In a preferred form of the invention the first layer 22 is a polymer blend of: (a) from about 25% to about 50%, more preferably from about 30% to about 40%, by weight of the first layer a first polyolefin selected from the group consisting of polypropylene and polypropylene copolymers, (b) from about 0% to about 50%, more preferably

्रिकृत अस्त

- 5 -

from about 5% to about 40%, by weight of the first layer a second polyolefin of an α-olefin containing polymer or copolymer and more preferably is an ethylene and α-olefin copolymer; (c) from about 0% to about 40%, more preferably from about 10% to about 40% of the first layer a radio frequency susceptible polymer selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, polyimides, polyurethanes; polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene methyl acrylate copolymers with methyl acrylate comonomer content from 12%-40% by weight of the copolymer, ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer; and (d) from about 0% to about 40%, more preferably from about 10% to about 40% of a thermoplastic elastomer by weight of the first layer.

5

10

15

20

25

30

The second layer 24 of the port tube 18 is of a non-PVC containing material that is capable of being solvent bonded to the membrane tube 20. In a preferred form of the invention the second layer 24 is a thermoplastic elastomer or a blend of a thermoplastic elastomer in an amount by weight of from about 80% to about 100% and a propylene containing polymer from about 0% to about 20% by weight of the second layer 24. It is also desirable, but optional, that the second layer 24 softens slightly at autoclave temperatures so that when the port tube and membrane tube assembly is steam sterilized, the port tube more tightly adheres to the membrane tube.

As shown in the Figures, the first layer has a thickness greater than the second layer. In a preferred form of the invention the first layer will have a thickness of from about 15 mils to about 40 mils and more preferably from about 20 mils to about 30 mils. The second layer will have a thickness from about 2 mils to about 10 mils and more preferably from about 3 mils to about 7 mils.

The membrane tube 20 should be fabricated from a non-PVC containing material and should be capable of being bonded to the port tube 18, preferably using solvent bonding techniques. Solvent bonding is well known in the art. Solvent bonding typically includes applying a solvent to a polymeric material to partially dissolve the polymer. While in this dissolved state the dissolved polymer material is placed in contact with a material, such as another polymer, that the polymeric material is to be bonded to. Suitable solvents for solvent bonding of the materials of the present invention include at least the following aromatic solvents: cyclohexane, cyclohexanone, toluene, tetrahydofuran, cumene, xylenes, diethyl benzene, decalin, tetralin and amyl benzene to name a few.

ंक चंद्र चंद्र स्थ

- 6 -

Accordingly, to solvent bond the membrane tube to the port tube, a portion of the membrane tube that is to be in contact with the port tube is exposed to the solvent, typically by dipping the relevant portion of the membrane tube into the solvent. Then the membrane tube is inserted into the membrane tube in telescoping fashion where a strong bond is formed.

5

10

15

20

25

30

In a preferred form of the invention, the membrane tube 20 is a multilayered structure having an outer layer 30, a core layer 32, and an inner layer 34. In a preferred form of the invention, the outer layer 30 is a polymer blend of: (a) from about 0% to about 60%, more preferably from about 20% to about 55% and most preferably from about 30% to about 50%, by weight of the outer layer of a polyolefin and (b) from about 40% to about 100%, more preferably from about 45% to about 80% and most preferably from about 50% to about 70%, by weight of the outer layer of a thermoplastic elastomer.

Also, in a preferred form of the invention, the core layer 32 is a polymer blend of: (a) from about 35% to about 100%, more preferably from about 50% to about 90% and most preferably 70% to about 90%, by weight of the core layer of a thermoplastic elastomer and (b) from about 0% to about 65%, more preferably from about 10% to about 50% and most preferably from about 10% to about 30%, by weight of the core layer of a polyolefin.

Also, in a preferred form of the invention, the inner layer 34 is a polymer blend of: (a) from about 25% to about 55%, more preferably from about 25% to about 40%, by weight of the inner layer a polyolefin; (b) from about 0% to about 50%, more preferably from about 0% to about 40% and most preferably 0% to about 20%, by weight of the inner layer a polyolefin selected from the group consisting of α-olefin containing polymers or copolymers and more preferably is an ethylene and α-olefin copolymer; (c) from about 0% to about 40% by weight, more preferably from about 15% to about 40%, of the inner layer a radio frequency susceptible polymer selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, polyimides, polyurethanes, polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene methyl acrylate comonomer content from 12%-40% by weight of the copolymer, ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer; and (d) from about 0% to about 40%, more preferably from about 15% to about 40%, by weight of the inner layer of a thermoplastic elastomer.

In a preferred form of the invention, the outer layer 30 will have a thickness from about 3 mils to about 15 mils and more preferably from about 3 mils to about 10 mils. The core layer 32

Ť

-7-

will have a thickness from about 10 mils to about 35 mils and more preferably from about 10 mils to about 30 mils. The inner layer 34 will have a thickness from about 3 mils to about 15 mils and more preferably from about 5 mils to about 10 mils.

5

10

15

20

25

30

Thermoplastic elastomers include styrene and hydrocarbon copolymers, EPDM, and ethylene propylene rubber. The styrene can be substituted or unsubstituted styrene. The styrene and hydrocarbon copolymers can be block copolymer including di-block, tri-block, star block, it can also be a random copolymer and other types of styrene and hydrocarbon copolymers that are known by those skilled in the art. Styrene and hydrocarbon copolymers therefore include for example, but are not limited to, styrene-butene-styrene block copolymer, styrene-ethylene-butene-styrene block copolymers, styrene-isobutene-styrene and the numerous other varieties of styrene and hydrocarbon copolymers can also be blends of various types of the above-identified styrene and hydrocarbon copolymers.

The styrene and hydrocarbon copolymers can be modified or functionalized by carboxylic acid groups, anhydrides of carboxylic acids, esters of carboxylic acids, epoxy groups and carbon monoxide. In a preferred form of the invention, the thermoplastic elastomer of the first layer 22 of the port tube 18 and the inner layer 34 of the membrane tube 20 is an SEBS copolymer with a maleic anhydride group in an amount by weight of about 2% or less. Such a copolymer is sold by Shell Chemical Company under the tradename KRATON® FG1924X and FG1901X.

The thermoplastic elastomer of the second layer 24 of the port tube 18 and the outer layer 30 of the membrane tube 20 is preferably a styrene and diene copolymer more preferably selected from the group consisting of styrene-ethylene-butene-styrene copolymers, and styrene-isoprene-styrene copolymers. More preferably the thermoplastic elastomer of the second layer is an ethylene butene copolymer, and more preferably a styrene-ethylene-butene-styrene copolymer. It has been found that such a copolymer is well suited for solvent bonding. Suitable SEBS copolymers are sold by Shell Chemical Company under the tradename KRATON® KG1657.

The thermoplastic elastomer of the core layer of the membrane tube is an SEBS copolymer containing a high proportion of triblock. Suitable polymers are sold by Shell Chemical Company under the tradename KRATON® KG1660, KG1652 and KG1650.

Suitable polypropylene polymers include homopolymers and copolymers. Suitable comonomers are  $\alpha$ -olefin s having from 2 to 17 carbons and most preferably is ethylene in an amount by weight from about 1 to about 8% by weight of the copolymer.

16 16 16

- 8 -

Suitable  $\alpha$ -olefin containing polymers include homopolymers, copolymers and interpolymers of  $\alpha$ -olefins having from 2 to 17 carbons. Suitable ethylene  $\alpha$ -olefin copolymers of the first layer 22 of the port tube 18 and the inner layer 34 of the membrane tube 20 have a density, as measured by ASTM D-792, of less than about 0.915 g/cc, more preferably less than about 0.905 g/cc, and are commonly referred to as very low density polylethylene (VLDPE), ultra low density polyethylene (ULDPE) and the like. In a preferred form of the invention, the ethylene and  $\alpha$ -olefin copolymers are obtained using a single site catalyst such as metallocene catalysts, vanadium catalysts and the like. Suitable catalyst systems, among others, are those disclosed in U.S. Patent Nos. 5,783,638 and 5,272,236. Suitable ethylene and  $\alpha$ -olefin copolymers include those sold by Dow Chemical Company under the AFFINITY tradename, Dupont-Dow under the ENGAGE tradename, Exxon under the EXACT tradename and Phillips Chemical Company under the tradename MARLEX.

The port tube assembly, in a preferred form of the invention satisfies the following physical properties: (1) has a spike insertion force of less than about 35 lbs on average, (2) has a spike removal force of greater than about 5 lbs on average. The pull force to separate the membrane tube from the port tube is greater than the spike removal force.

The following is a non-limiting example of the present invention.

4fi

(in

ंह

:3

#### **Examples:**

5

10

15

20

25

30

A two layered port tube having an outer and an inner layer was coextruded. The inner layer had a thickness of 0.006 inches and was fabricated from SEBS. The outer layer had a thickness of 0.026 inches and was fabricated from a polymer blend by weight of the outer layer of 35% polypropylene/5% ultra low density polyethylene/30% dimer fatty acid polyamide/30% SEBS with maleic anhydride functionality.

A three layered membrane tube was coextruded having an inner layer, a core layer and an outer layer. The inner layer is a polymer blend by weight 30% polypropylene/35% dimer fatty acid polyamide/35% SEBS. The core layer was a blend of 85% SEBS and 15% polypropylene. The outer layer was 45% SEBS and 55% polypropylene. The inner layer had a thickness of 0.003 inches, the core layer 0.023 inches and the outer layer 0.006 inches.

Polymeric sheeting was extruded from a blend by weight of 10% dimer fatty acid polyamide, 35% ultra low density polyethylene, 45% polypropylene and 10% SEBS with maleic anhydride functionality.

Two rectangularly-shaped sheets of the polymeric sheeting were placed into registration and

- 9 -

. :

sealed along 3 peripheral edges to define a pouch. A port tube segment was inserted into an open end of the pouch and was heat sealed therein while sealing the final peripheral edge to define a container. A membrane tube segment was dipped into cyclohexanone and inserted in a telescoping fashion into the port tube segment.

5

10

15

20

The container was bolted down proximate a mechanical tester. The port tube was attached to a spike attached to a cross-head of the mechanical tester. The cross-head speed of the tester was set at 20 in/min. The cross-head was set to achieve the desired spike insertion depth in the port tube. The tester allowed for measuring the spike insertion force and the spike removal force. The average spike insertion value after 50 tests was 13.31 lbf. The average spike removal force for 50 tests was 10.37 lbf. These measurements were made after the spike dwelled in the membrane tube for 24 hours.

The tester was also used to determine the pull force necessary to remove the port tube from the container or to otherwise damage the container or port tube. The port tube was inserted into the tester with the container bolted down. The average pull force for 28 tests was 30.04 lbf. This test was conducted prior to steam sterilizing the container. The value for 30 test after the container was steam sterilized was 42.68 lbf.

From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the spirit and scope of the invention. It is to be understood that no limitation with respect to the specific apparatus illustrated herein is intended or should be inferred. It is, of course, intended to cover by the appended claims all such modifications as fall within the scope of the claims.

17

ì

Ġ

)ŠĒ

#### **CLAIMS**

#### WE CLAIM:

1. A multiple layered non-PVC containing tubing comprising:

a first layer of a polymer blend of: (a) from about 25% to about 50% by weight of the first layer a first polyolefin selected from the group consisting of polypropylene and polypropylene copolymers, (b) from about 0 to about 50% by weight of the first layer a second polyolefin selected from the group consisting of ethylene copolymers, ultra-low density polyethylene, polybutene, polybutadiene and butene ethylene copolymers; (c) from about 0% to about 40% by weight of the first layer a radio frequency susceptible polymer selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, polyimides, polyurethanes, polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene methyl acrylate copolymers with methyl acrylate comonomer content from 12%-40% by weight of the copolymer, ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer; (d) from about 0% to about 40% of a first thermoplastic elastomer; and

a second layer disposed coaxially within the first layer and being a second thermoplastic elastomer.

- 2. The tubing of claim 1 wherein the polyamide is selected from a group consisting of: aliphatic polyamides resulting from the condensation reaction of diamines having a carbon number within a range of 2-13, aliphatic polyamides resulting from a condensation reaction of di-acids having a carbon number within a range of 2-13, polyamides resulting from the condensation reaction of dimer fatty acids, and amide containing copolymers.
- 3. The tubing of claim 1 wherein the polyamide is a dimer fatty acid polyamide.
- 4. The tubing of claim 1 wherein the first polyolefin is a propylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons.
- 5. The tubing of claim 4 wherein the first polyolefin is a propylene and ethylene copolymer having an ethylene content of from about 1% to about 8% by weight of the first polyolefin.
- 6. The tubing of claim 1 wherein the first thermoplastic elastomer is selected from the group consisting of a first styrene and hydrocarbon copolymer.
- 7. The tubing of claim 6 wherein the first styrene and hydrocarbon copolymer is selected from the group of polymers structures with diblock, triblock, radial block, and star block.
- 8. The tubing of claim 7 wherein the first thermoplastic elastomer is a styrene-ethylene-butene-

::3-

styrene block copolymer.

- 9. The tubing of claim 7 wherein the first thermoplastic elastomer is functionalized with a group selected from the group consisting of carboxylic acid, esters of carboxylic acids, anhydrides of carboxylic acids, epoxides, and carbon monoxide.
- 10. The tubing of claim 9 wherein the first thermoplastic elastomer is maleic anhydride functionalized.
- 11. The tubing of claim 1 wherein the second thermoplastic elastomer is selected from the group consisting of a second styrene and hydrocarbon copolymer.
- 12. The tubing of claim 11 wherein the second styrene and hydrocarbon copolymer is selected from the group of polymer structures with diblock, triblock, radial block, and star block.
- 13. The tubing of claim 12 wherein the second thermoplastic elastomer is selected from the group consisting of a styrene-ethylene-butene-styrene copolymer, styrene-isoprene-styrene and styrene-ethylene-propylene.
- 14. The tubing of claim 13 wherein the second thermoplastic elastomer contains styreneethylene-butene-styrene diblock copolymer and a styrene-ethylene-butene-styrene triblock copolymer.
- 15. The tubing of claim 1 wherein the second polyolefin is an ethylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefins.
- 16. The tubing of claim 15 wherein the ethylene and  $\alpha$ -olefin copolymer is obtained using a single-site catalyst.
- 17. The tubing of claim 1 wherein the second layer further comprises an additive selected from the group consisting of polypropylene, high density polyethylene, silica, slip agents, fatty amides, and acrawax.
- 18. The tubing of claim 17 wherein the additive is present in an amount by weight of the second layer from about 0% to about 20%.
- 19. A multiple layered non-PVC containing tubing comprising:

an outer layer of a polymer blend of: (a) from about 0% to about 60% by weight of the outer layer of a first polyolefin and (b) from about 40% to about 100% by weight of the outer layer of a first thermoplastic elastomer;

a core layer attached to the outer layer, the core layer is a polymer blend of: (a) from about 35% to about 100% by weight of the core layer of a second thermoplastic elastomer and (b) from about 0% to about 65% by weight of the core layer of a second polyolefin; and

· '}} · · i:

 $\cdot \cdot \cdot \cdot$ 

ž.

an inner layer attached to the core layer on a side opposite of the outer layer, the inner layer being a polymer blend of: (a) from about 25% to about 55% by weight of the inner layer a third polyolefin, (b) from about 0 to about 50% by weight of the inner layer a fourth polyolefin selected from the group consisting of ethylene copolymers, ultra-low density polyethylene, polybutene, and butene ethylene copolymers; (c) from about 0% to about 40% by weight of the inner layer a radio frequency susceptible polymer selected from the group consisting of polyamides, ethylene acrylic acid copolymers, ethylene methacrylic acid copolymers, polyimides, polyurethanes, polyesters, polyureas, ethylene vinyl acetate copolymers with a vinyl acetate comonomer content from 12%-50% by weight of the copolymer, ethylene methyl acrylate copolymers with methyl acrylate comonomer content from 12%-40% by weight of the copolymer, ethylene vinyl alcohol with vinyl alcohol comonomer content from 12%-70% by mole percent of the copolymer; and (d) from about 0% to about 40% by weight of the inner layer of a third thermoplastic elastomer.

- 20. The tubing of claim 19 wherein the polyamide is selected from a group consisting of: aliphatic polyamides resulting from the condensation reaction of diamines having a carbon number within a range of 2-13, aliphatic polyamides resulting from a condensation reaction of di-acids having a carbon number within a range of 2-13, polyamides resulting from the condensation reaction of dimer fatty acids, and amide containing copolymers.
- 21. The tubing of claim 19 wherein the polyamide is a dimer fatty acid polyamide.
- 22. The tubing of claim 19 wherein the first polyolefin is selected from the group consisting of a polypropylene homopolymer, a propylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons, ethylene homopolymers and ethylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons.
- 23. The tubing of claim 22 wherein the first polyolefin is a propylene and ethylene copolymer having an ethylene content of from about 1% to about 8% by weight of the first polyolefin.
- The tubing of claim 19 wherein the second polyolefin is selected from the group consisting of a polypropylene homopolymer, a propylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons, ethylene homopolymers and ethylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons.
- 25. The tubing of claim 19 wherein the third polyolefin is selected from the group consisting of a polypropylene homopolymer, a propylene copolymerized with a monomer selected from the

- 13 -

group consisting of  $\alpha$ -olefin s having from 2-17 carbons, ethylene homopolymers and ethylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefin s having from 2-17 carbons..

- 26. The tubing of claim 19 wherein the first thermoplastic elastomer is selected from the group consisting of a first styrene and hydrocarbon copolymers.
- 27. The tubing of claim 26 wherein the first styrene and hydrocarbon copolymer is selected from the group of polymers structures with diblock, triblock, radial block, and star block.
- 28. The tubing of claim 27 wherein the first thermoplastic elastomer is selected from a first styrene-ethylene-butene-styrene copolymer, styrene-isoprene-styrene copolymer and styrene-ethylene-propylene-styrene copolymer.
- 29. The tubing of claim 28 wherein the first thermoplastic elastomer is a styrene-ethylene-butene-styrene diblock copolymer and a styrene-ethylene-butene-styrene triblock copolymer.
- 30. The tubing of claim 19 wherein the second thermoplastic elastomer is selected from the group consisting of a second styrene and hydrocarbon copolymers.
- 31. The tubing of claim 30 wherein the second styrene and hydrocarbon copolymer is selected from the group consisting of a polymer structure with diblock, triblock, copolymers, styrene and hydrocarbon star block copolymers, and blends containing the same.
- 32. The tubing of claim 31 wherein the second thermoplastic elastomer is selected from a second styrene-ethylene-butene-styrene copolymer, a second styrene-isoprene-styrene copolymer and a second styrene-ethylene-propylene-styrene copolymer.
- 33. The tubing of claim 19 wherein the third thermoplastic elastomer is selected from the group consisting of a third styrene and hydrocarbon copolymers.
- 34. The tubing of claim 33 wherein the third styrene and hydrocarbon copolymer is selected from the group consisting of polymer structure with diblock, triblock, star block copolymers and blends of the same.
- 35. The tubing of claim 34 wherein the third thermoplastic elastomer is a third styrene-ethyleness butene-styrene block copolymer.
- 36. The tubing of claim 34 wherein the third thermoplastic elastomer is functionalized with a group selected from the group consisting of carboxylic acid, esters of carboxylic acids, anhydrides of carboxylic acids, epoxides, and carbon monoxide.
- 37. The tubing of claim 36 wherein the third thermoplastic elastomer is maleic anhydride functionalized.

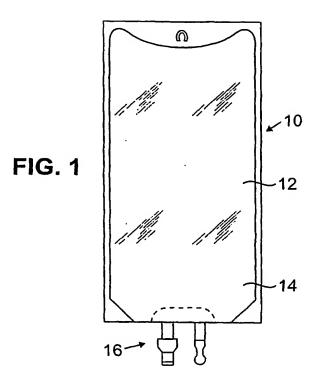
÷

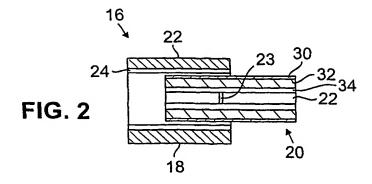
.,1

: 5:

: 1

- 38. The tubing of claim 19 wherein the fourth polyolefin is an ethylene copolymerized with a monomer selected from the group consisting of  $\alpha$ -olefins.
- 39. The tubing of claim 38 wherein the fourth polyolefin is an ethylene and  $\alpha$ -olefin copolymer.
- 40. The tubing of claim 39 wherein the ethylene and  $\alpha$ -olefin copolymer is obtained using a single-site catalyst.





inte | bnai Application No PCT/US 02/00299

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B32B1/08 B290 A61L29/12 B29C65/04 C08L23/10 According to International Patent Classification (IPC) or to both national classification and IPC Minimum documentation searched (classification system followed by classification symbols) A61L B29C B29D B32B C08L F16L IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to daim No. Υ WO 95 13918 A (BAXTER INT) 1-18 26 May 1995 (1995-05-26) page 1, paragraph 1 - paragraph 2; claims 1-55; figures 1-10 EP 0 765 740 A (FRESENIUS AG) 1 - 182 April 1997 (1997-04-02) claims 1.4 Α US 5 529 821 A (ISHIKAWA KENJI ET AL) 1 25 June 1996 (1996-06-25) claim 43; example 1 Α US 6 004 311 A (HEILMANN KLAUS ET AL) 19 21 December 1999 (1999-12-21) claim 1; figure 1 -/--Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but died to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-ments, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or document published prior to the international filling date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the International search Date of mailing of the international search report 14 May 2002 27/05/2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016 Van Nieuwenhuize, O

Form PCT/ISA/210 (second sheet) (July 1992)

Inte lonal Application No PCT/US 02/00299

		PC1/US 02/00299	
C.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
A	EP 1 059 479 A (MEIJI GOMU KASEI KK ;KONDO TAKESHI (JP); ISHII TOSHINORI (JP); TAN) 13 December 2000 (2000-12-13) claim 1	1	
A	US 5 562 127 A (KO JOHN H ET AL) 8 October 1996 (1996-10-08) claim 1; figure 1	1	
A	EP 0 623 651 A (WENDELBORN DIETER ;SCHAEFER HELMUT (DE); MOLTRECHT WILFRIED (DE)) 9 November 1994 (1994–11–09) claim 1	1,4-8	
A	EP 0 564 231 A (GRACE W R & CO) 6 October 1993 (1993-10-06) claims 1,2	1	
Α	US 4 588 777 A (HOTTA MASAHIRO) 13 May 1986 (1986-05-13) example 6	1.	
A	US 5 601 889 A (CHUNDURY DEENADAYALU ET AL) 11 February 1997 (1997-02-11) claim 1 	1	
			٠
			,
			,
		}	- 27

ormation on patent family members

Inte onal Application No
PCT/US 02/00299

				FC1703	02/00299	
Patent document atted in search repo	rt	Publication date		Patent family member(s)	Publication date	•
WO 9513918	A	26-05-1995	US	5998019 A	07-12-1999	•
			AT	175383 T	15-01-1999	•
			AU	686285 B2	05-02-1998	
			AU	1182395 A	06-06-1995	
			BR CA	9405785 A 2153481 Al	12-12-1995 26-05-1995	
			CN	1117718 A ,B	28-02-1996	
			CZ	9501746 A3	17-01-1996	
			DE	69415792 D1	18-02-1999	
			DE	69415792 T2	19-08-1999	
			DK	679124 T3	30-08-1999	
			EP	0679124 A1	02-11-1995	
			ES	2129189 T3	01-06-1999	
			GR	3029456 T3	28-05-1999	
			HK	1002389 A1	16-06-2000	•
			HU	72715 A2	28-05-1996	
			JP	8506068 T	02-07-1996	
			NO	952802 A	15-09-1995	
			NZ	276958 A	27-04-1998	
			PL	309919 A1	13-11-1995	
			SG	65537 A1	22-06-1999	
			TR	27954 A	06-11-1995 26-05-1995	
			WO US	9513918 A1 6168862 B1	02-01-2001	
			US	6261655 B1	17-07-2001	
			US	5993949 A	30-11-1999	
			ZA	9408817 A	11-07-1995	
EP 0765740	A	02-04-1997	DE	19534455 C1	12-12-1996	
LI 0703740	••	02 04 1337	AU	699497 B2	03-12-1998	
			AU	6213496 A	20-03-1997	
			BR	9603732 A	26-05-1998	
			CA	2184868 A1	17-03-1997	
			EP	0765740 A2	02-04-1997	
			JP	9123314 A	13-05-1997	
			US	5928744 A	27-07-1999	
US 5529821	Α	25-06-1996	DE	69329783 D1	01-02-2001	
			DE	69329783 T2	05-07-2001	
			EP	0577493 A2	05-01-1994	
			JP	3233738 B2	26-11-2001	
			JP	6070971 A	15-03-1994	
US 6004311	Α	21-12-1999	DE	19534413 C1	28-05-1997	
			AU	707219 B2	08-07-1999	
			AU	6430096 A	20-03-1997	
			BR	9603731 A	26-05-1998	
	•		CA	2184869 A1	17-03-1997	
	•		EP JP	0769516 A2 9103493 A	23-04-1997 22-04-1997	
EP 1059479	Α	13-12-2000	JP	2001349476 A	21-12-2001	
			ΑU	1691000 A	24-07-2000	
			EP	1059479 A1	13-12-2000	
			CN WO	1294668 T 0040884 A1	09-05-2001 13-07-2000	
	A	08-10-1996	AU	7327894 A	28-02-1995	•

muormation on patent family members

Inte Jonal Application No PCT/US 02/00299

Patent document cited in search report	Publication date	Patent family member(s)		Publication date	
US 5562127 A			712354 A1 504652 A1	22-05-1996 16-02-1995	
EP 0623651 A	09-11-1994	AT DE 59 EP 0	315003 A1 161564 T 404856 D1 623651 A2 113012 T3	10-11-1994 15-01-1998 05-02-1998 09-11-1994 16-04-1998	
EP 0564231 A	06-10-1993	DE 69 DE 69 EP 0 ES 2 JP 6	152964 T 2091306 A1 2310601 D1 2310601 T2 2564231 A1 2103429 T3 5048451 A	15-05-1997 01-10-1993 19-06-1997 11-09-1997 06-10-1993 16-09-1997 22-02-1994 05-10-1993	
US 4588777 A	13-05-1986	JP 59 JP 63 BE DE 3 GB HK SE	463605 C 9074153 A 8009546 B 904955 A7 8337997 A1 2131816 A ,B 72190 A 458859 B 8305686 A 51189 G	28-10-1988 26-04-1984 29-02-1988 16-10-1986 26-04-1984 27-06-1984 21-09-1990 16-05-1989 30-05-1984 02-03-1990	
US 5601889 A	11-02-1997	EP (	2136106 A1 0642550 A1 9324568 A1	30-11-1993 15-03-1995 09-12-1993	